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(54) **SULPHUR FREE COMPOSITION AND LUBRICANT COMPOSITION AND METHODS THEREOF**

SCHWEFELFREIE ZUSAMMENSETZUNG UND SCHMIERMITTELZUSAMMENSETZUNG UND VERFAHREN DAVON

COMPOSITION EXEMPTÉ DE SOUFRE, COMPOSITION LUBRIFIANTE ET PROCÉDES ASSOCIÉS

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DescriptionBACKGROUND OF THE INVENTION

5 1. Field of the Invention

[0001] This invention involves a sulphur free composition, a composition containing the sulphur free composition and an oil of lubricating viscosity, and methods to prepare and use the sulphur free composition. The sulphur free composition is especially useful in lubricants for an internal combustion engine by providing multifunctional performance without introducing sulphur and introducing at most only minor amounts of metal into the lubricant.

2. Description of the Related Art

[0002] Detergents are lubricant additive compositions that typically provide detergency performance to a lubricant composition that can include neutralizing acids, preventing corrosion, and providing cleanliness by suspending deposit forming substances and removing deposits. Detergents generally consist of an anionic organic surfactant portion that usually contains sulphur such as an alkylarylsulphonate, a cationic metal counterion, and a basic metal salt in a colloidal suspension that provides a base reserve for neutralizing acids. Various lubricant compositions such as certain two-stroke engine oils and stationary natural gas engine oils require detergency performance, but also require that the engine oil contain little or no metals for satisfactory performance. Dispersants provide cleanliness to all types of lubricant compositions by suspending deposit forming substances.

[0003] It is also well known for lubricating oils to contain a number of additives used to protect the engine from wear, the accumulation of deposits, and filter plugging. Common additives for engine lubricating oils include zinc dialkyldithiophosphates (ZDDP) as antiwear additives and alkali and alkaline earth metal overbased sulphonate and phenate detergents. It is believed that ZDDP antiwear additives protect the engine by forming a protective film on metal surfaces. Typical treatment quantities of ZDDP range from 1 to 2 weight percent based on the total weight of the lubricant. Detergents such as overbased calcium sulphonates help keep the engine parts clean of deposits and offer an alkalinity reserve. Typical treatment quantities of detergents range from 0.05 to 10 weight percent based on the total weight of the lubricant.

[0004] Current and future regulations regarding exhaust emissions from internal combustion engines that contain exhaust treatment devices are requiring a reduction in the sulphur, phosphorus and metal content of engine oils used in these engines. This reduction in the sulphur, phosphorus and metal content of engine oils is being implemented because it is thought that they can adversely affect the performance of exhaust treatment devices.

[0005] Any reduction in the performance of catalytic converters tends to result in increased amounts of greenhouse gases such as nitric oxide and/or sulphur oxides. However, reducing the amount of ZDDP will increase the amount of wear in an engine. Also reducing the amount of detergent will decrease engine cleanliness and result in increased deposits.

[0006] International Publication No. WO-A-03/18728 (Moreton et al.) discloses a linear compound containing phenolic and salicylic units and a metal salt or boron-containing metal salt thereof and use of the compound and the salts in a lubricating oil composition.

[0007] International Publication No. WO-A-01/56968 (Taylor et al.) discloses a cyclic compound for use in a fuel and a lubricating oil composition where the cyclic compound comprises carboxyl-substituted and/or hydroxyl-substituted aromatic units joined together to form a ring and the carboxyl substituent can be present as an acid or as a carboxylic salt with a metal or ammonium cation.

[0008] U. S.-A-5,688,751 (Cleveland et al.) discloses a mixture of an oil of lubricating viscosity and a hydrocarbyl-substituted hydroxyaromatic carboxylic acid or an ester, amide, ammonium or amine salt, or monovalent metal salt thereof for lubrication of two-stroke cycle engines.

[0009] U.S.-A-6,310,009 (Kocsis et al.) discloses a saligenin derivative and a lubricating oil composition comprising the saligenin derivative.

[0010] U. S.-A-5,202,038 (Schoch et al.) discloses salts which can be used as antiwear additives for lubricants and which are formed by a fatty amine with a mixture of a monocarboxylic acid and a dicarboxylic acid where the acids contain a perfluoroalkyl radical.

[0011] US-A-5,827,805 discloses reaction products of polyisobutyl substituted phenol, glyoxal and N,N-dimethylamine propylamine (Example 27) and a polyamine bottoms mixture (Example 28).

[0012] WO-A-02/072529 discloses a lubricant or fuel additive which is a linear condensed product based on alkyl phenol and salicylic acid.

[0013] Tetrabutylammonium hydroxide is used in the preparation in amounts that are higher than catalytic and the end product contains nitrogen. It refers to deposit formation and to removal of black paint and it also refers to the use

of the compounds in engines.

[0014] It has now been found that the composition of the present invention provides detergency, antiwear and dispersancy performance to a composition such as an engine oil and is free of sulphur and metals or contains only a minor amount of metals.

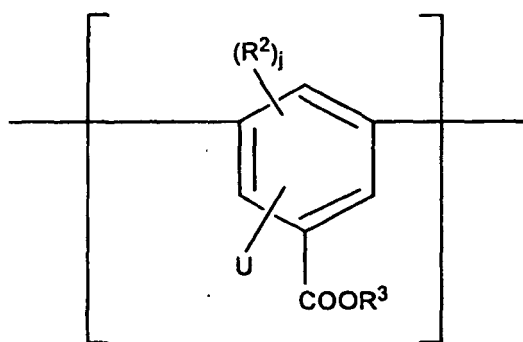
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SUMMARY OF THE INVENTION

[0015] The present invention provides a composition comprising:

- 10 (a) a sulphur free reaction product of:
- (i) a hydrocarbyl substituted aromatic compound containing an acidic group selected from the group consisting of a carboxylic group, a hydroxyl group and mixtures thereof; and
 - (ii) an organic nitrogen-containing base reacted with the acidic group; and
- 15 (b) an oil of lubricating viscosity,
wherein (a)(i) is a substantially linear compound comprising at least one unit of the formula (I)

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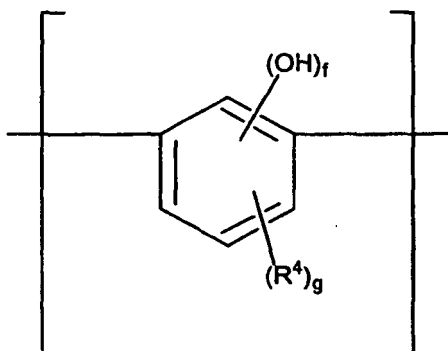
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(I)

or the formula (II)

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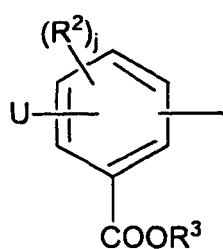
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(II)

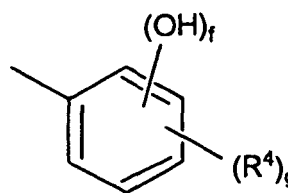
wherein each end of the compound is terminated by a unit of the formula (III) or the formula (IV)

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(III)



(IV)

and wherein the units of the compound are linked by divalent bridging groups which may be the same or different for each linkage; U is a hydroxyl group for (a)(i)(1), or is selected from the group consisting of $-\text{NH}_2$, $-\text{NHR}^1$, $-\text{N}(\text{R}^1)_2$ and mixtures thereof for (a)(i)(2), wherein R^1 is a hydrocarbyl group containing 1 to 5 carbon atoms; R^2 is a hydroxyl or a hydrocarbyl group and j is 0, 1 or 2; R^3 is hydrogen or a hydrocarbyl group; f is 1, 2 or 3; R^4 is a hydrocarbyl group or a substituted hydrocarbyl group and g is 1, 2 or 3 provided that at least one R^4 group contains 8 or more carbon atoms; and wherein the compound on average contains at least one unit of formula (I) or (III) and at least one unit of formula (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the compound is 0.1:1 to 2: 1.

[0016] The invention further provides a process for the preparation of the above composition comprising:

- (a) heating reactants (a)(i) and (a)(ii) as described above and hereinbelow;
- (b) optionally holding the product of step (a) under vacuum; and
- (c) adding the product of step (a) or (b) to an oil of lubricating viscosity.

[0017] The invention also provides a use of the inventive composition for imparting to an internal combustion engine an improvement in one or more performance properties selected from the group selected consisting of cleanliness, wear and exhaust emissions.

[0018] The invention additionally provides a method of lubricating and of improving the performance of an internal combustion engine comprising supplying to the engine a lubricant composition comprising the sulphur free reaction product of components (a)(i) and (a)(ii) as described throughout this application. Preferred embodiments of the invention are apparent from the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The present invention provides a composition as mentioned above.

[0020] Throughout this application the term hydrocarbyl represents a univalent group of one or more carbon atoms that is predominately hydrocarbon in nature, but can contain heteroatoms such as oxygen in the carbon chain and can have nonhydrocarbon and heteroatom-containing groups such as hydroxy, halo, nitro and alkoxy attached to the carbon chain.

[0021] Component (a) of the composition of this invention in addition to being free of sulphur can be free of a metal by having no sulphated ash, as determined by American Society for Testing and Materials specification ASTM D-874, or can contain a minor amount of metal by having a sulphated ash on a weight basis below 0.5%, below 0.25% or below 0.1%.

[0022] Often the composition has a total base number (TBN). Often the TBN of the composition is 3 or higher, in one aspect 5 or higher, and in yet another aspect 9 or higher.

[0023] Component (a) of the composition is often present on a weight basis at 0.01 to 40%, in another aspect at 0.5 to 40%, in yet another aspect at 0.75 to 20% and yet another aspect at 1 to 15% of the composition.

(a)(i) is at least one member selected from the group consisting of (1) an oligomeric reaction product of an hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenol; (2) an oligomeric reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenylamine.

[0024] In one embodiment of the invention (a)(i) is an oligomeric species, and in other embodiments (a)(i) is (a)(i)(1), (a)(i)(2), or a mixture thereof. In another embodiment of the invention the carboxylic or carboxyl group substituted on a phenol or phenylamine of this invention is an acid group $-\text{CO}_2\text{H}$, and in other embodiments is an ester group $-\text{CO}_2\text{R}$

where R is a hydrocarbyl group or is a mixture of acid and ester groups.

[0025] Often (a)(ii) is at least one member selected from the group consisting of (1) an amino-containing imine or a reactive equivalent thereof; (2), a monoamine; (3) a polyamine; (4) a nitrogen containing heterocycle; (5) an aminoalcohol; (6) a tetraalkylammonium salt; and (7) a non-heterocyclic aromatic amine.

[0026] The invention further provides a composition comprising:

(a) a sulphur free reaction product of:

- (i) a hydrocarbyl substituted aromatic compound containing a carboxyl and/or hydroxyl acidic group and selected from the group consisting of (1) an oligomeric reaction product of an hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenol; (2) an oligomeric reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenylamine; and mixtures thereof; and
- (ii) an organic nitrogen-containing base reacted with the acidic group of (a)(i).

Hydrocarbyl Substituted Aromatic Compound

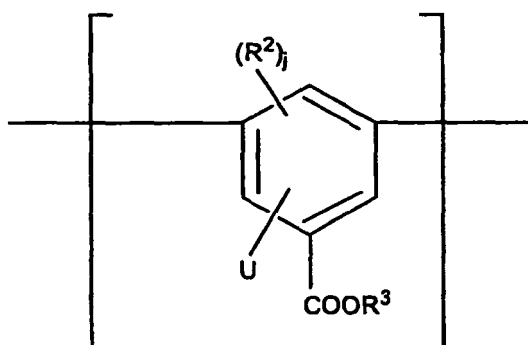
[0027] The hydrocarbyl substituent of the hydrocarbyl-substituted phenol of the reactant (a)(i)(1) or (a)(i)(2) may have 1 to 60 carbon atoms, in another aspect 4 to 50 carbon atoms, and in a further aspects 6 to 40 or 7 to 30 carbon atoms. The hydrocarbyl substituent is often alkyl and in another aspect is derived from an olefin. The alkyl substituent is often derived from a polyolefin which may be a homopolymer from one olefin monomer or a copolymer from a mixture of two or more olefin monomers. The olefin monomer may be an alpha-olefin, an internal olefin, or a polyene and includes ethylene, propylene, butene isomers, pentene isomers, decene isomers, and dienes. Useful polyolefins are polypropylenes and polyisobutylenes. Methods to prepare the polyolefins and the alkylphenols via alkylation of phenol with olefins or polyolefins are well known.

[0028] The aldehyde of the reactant of (a)(i)(1) or (a)(i)(2) may have 1 to 6 carbon atoms. The aldehyde may be formaldehyde in one of its reactive forms such as formalin or paraformaldehyde. The carboxyl-substituted phenol of the reactant of (a)(i)(1) may be a 2- or 3- or 4-hydroxybenzoic acid or a dihydroxybenzoic acid such as 3,5-dihydroxybenzoic acid. The carboxyl substituted phenol may have alkyl substituents. A useful carboxyl-substituted phenol is salicylic acid. The carboxyl substituted phenylamine of the reactant (a)(i)(2) is normally anthranilic acid and can contain additional alkyl, hydroxyl or amino substituents. The oligomeric reaction product of (a)(i)(1) or (a)(i)(2) contains at least one hydrocarbyl-substituted phenol unit and at least one carboxyl-substituted phenol or carboxyl-substituted phenylamine unit. The oligomeric reaction product of (a)(i)(1) or (a)(i)(2) may contain 2 to 20 phenol or phenylamine units, 2 to 10 phenol or phenylamine units, or 2 to 8 phenol or phenylamine units. The oligomeric reaction product of (a)(i)(1) or (a)(i)(2) may include linear molecules, cyclic molecules, or mixtures thereof. In an embodiment of the invention the oligomeric reaction product of (a)(i)(1) or (a)(i)(2) is a mixture of linear and cyclic molecules, and in another embodiment the mixture contains a majority of linear molecules.

[0029] The oligomeric reaction products of (a)(i)(1) and (a)(i)(2) may be prepared as described in U. S.-A-6,200,936 and/or in Preparative Examples A-E hereinbelow using a basic catalyst and a solvent. Basic catalysts include alkali and alkaline earth metal bases and amines such as lithium hydroxide, sodium hydroxide, potassium hydroxide and ammonium hydroxide. A solvent may be employed in the preparation of the oligomeric reaction product of (a)(i)(1) or (a)(i)(2) up to 90% by weight of the reaction mixture. The mole ratio of the hydrocarbyl-substituted phenol to the carboxyl-substituted phenol or phenylamine is often in the range from 1:0.05 to 1:19, and in a further embodiment of the invention is about 2 hydrocarbyl-substituted phenols to 1 carboxyl-substituted phenol or phenylamine. The mole ratio of combined hydrocarbyl-substituted phenol and carboxyl-substituted phenol or phenylamine to aldehyde may be 1:0.5-3.

[0030] The oligomeric reaction products of (a)(i)(1) and (a)(i)(2) are substantially linear compound comprising at least one unit of the formulae (I) or (II), provided U is -OH for (a)(i)(1) and U is selected from the group consisting of -NH₂, -NHR¹, -N(R¹)₂ and mixtures thereof for (a)(i)(2):

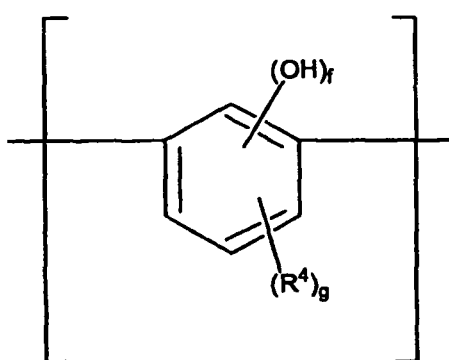
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(I)

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15 or



(II)

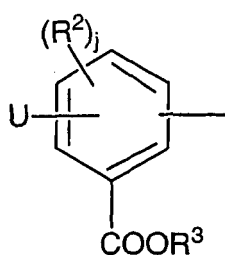
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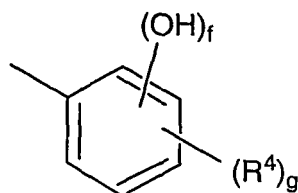
each end of the compound having a terminal group of formulae (III) or (IV):

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(III)

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(IV)

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such groups being linked by divalent bridging groups, which may be the same or different for each linkage; wherein f is 1, 2 or 3, in one aspect 1 or 2; R^1 is a hydrocarbyl group containing 1 to 5 carbon atoms; R^2 is hydroxyl or a hydrocarbyl group and j is 0, 1, or 2; R^3 is hydrogen or a hydrocarbyl group; R^4 is a hydrocarbyl group or a substituted hydrocarbyl group; g is 1, 2 or 3, provided at least one R^4 group contains 8 or more carbon atoms; and wherein the compound on average contains at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is about 0.1:1 to about 2:1.

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[0031] The U group in formulae (I) and (III) may be located in one or more positions ortho, meta, or para to the $-\text{COOR}^3$ group. In one aspect the U group is located ortho to the $-\text{COOR}^3$ group. When the U group is a $-\text{OH}$ group, formulae (I) and (III) are derived from 2-hydroxybenzoic acid (often called salicylic acid), 3-hydroxybenzoic acid, 4-hydroxybenzoic acid or mixtures thereof. When U is a $-\text{NH}_2$ group, formulae (I) and (III) are derived from 2-aminobenzoic acid (often called anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic acid or mixtures thereof.

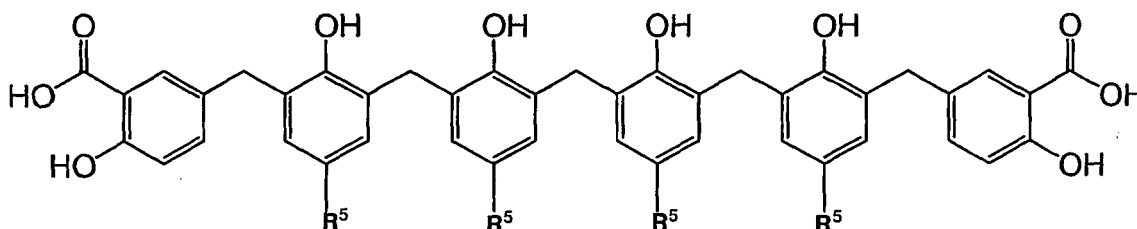
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[0032] The divalent bridging group, which may be the same or different in each occurrence, includes a methylene bridge such as $-CH_2-$ or $-CH(R)-$ and an ether bridge such as $-CH_2OCH_2-$ or $-CH(R)OCH(R)-$ where R is an alkyl group having 1 to 5 carbon atoms and where the methylene and ether bridges are derived from formaldehyde or an aldehyde having 2 to 6 carbon atoms.

[0033] Often the terminal group of formulae (III) or (IV) contains 1 or 2 hydroxymethyl groups ortho to a hydroxy group. Often the hydroxymethyl groups are present from 0 to 30 wt % of (a)(i)(1) and/or (a)(i)(2), in one aspect 0.1 to 20 wt % of (a)(i)(1) and/or (a)(i)(2), in another aspect 0.2 to 10 wt % of (a)(i)(1) and/or (a)(i)(2) and in yet another aspect 0.3 to 5 wt % of (a)(i)(1) and/or (a)(i)(2). In one embodiment of the invention hydroxymethyl groups are present. In one embodiment of the invention hydroxymethyl groups are not present.

[0034] In an embodiment of the invention the sulphur free reaction product of component (a) as described throughout this application can be a reaction product of components (a)(i), (a)(ii) and (a)(iii) a metal-containing base. The metal-containing base can be any reactive inorganic metal compound or mixture of compounds to include alkali and alkaline earth metal compounds such as oxides, hydroxides and carbonates like calcium hydroxide. The ratio of equivalents of (a)(i) to moles of (a)(ii) to equivalents of (a)(iii) can be respectively 1:0.25-2:0.25-2, and in other instances can be 1:0.25-1.5:0.5-2 or 1:0.4-1:1-1.7. In a further embodiment of the invention the reaction product of (a)(i), (a)(ii) and (a)(iii) is combined with an oil of lubricating viscosity or with an oil of lubricating viscosity and at least one other performance additive as described hereinbelow. The reaction product of (a)(i), (a)(ii) and (a)(iii) can be prepared as described in Example 14 below.

[0035] It is believed prior to neutralization that a significant fraction of the molecules of the oligomeric reaction product of component (a)(i)(1), as described above, can be represented on average by the following formula (V):



(V)

wherein each R^5 may be the same or different and is hydrogen or an alkyl group provided at least one R^5 is alkyl. In an embodiment R^5 is derived from a polyisobutylene having a number average molecular weight of 200 to 5000, and in other instances of 300 to 1000 and 400 to 700. Significant amounts of di- or trinuclear species may also be present containing one or two salicylic end groups of formula (III). The neutralized oligomeric reaction product of component (a)(i)(1) may be used alone or with other detergents.

[0036] The organic nitrogen-containing base of the present invention may be (a)(ii)(1) an amino-containing imine, a reactive equivalent thereof, or mixtures thereof. The amino-containing imine may be at least one selected from guanidine, aminoguanidine, 1,3-diaminoguanidine, formamidine, benzamidine, 3- or 4-aminobenzamidine, acetamidine, and reactive equivalents thereof. Reactive equivalents of this imine may be salts of the imine with acids to include hydrogen chloride, carbonic acid, and carboxylic acids such as formic acid and acetic acid. Examples of reactive equivalents of the imines are guanidine carbonate, aminoguanidine bicarbonate, or acetamidine hydrogen chloride.

[0037] The monoamine of (a)(ii)(2) often includes a hydrocarbyl-substituted primary, secondary or tertiary monoamine or mixture thereof. Often the hydrocarbyl group is an alkyl group. Each hydrocarbyl group often contains 1 to 40 carbon atoms, in another aspect 4 to 30 carbon atoms and in yet another aspect 6 to 20 carbon atoms. The hydrocarbyl group may be substituted or unsubstituted, branched or unbranched and in one aspect the hydrocarbyl group is unsubstituted. Examples of a suitable monoamine include methylamine, ethylamine, diethylamine, triethylamine, butylamine, dibutylamine, triethylamine, hexylamine, dihexylamine, trihexylamine, 2-ethylhexylamine, di(2-ethylhexyl)amine, tri(2-ethylhexyl)amine, nonylamine, dinonylamine, trinonylamine, dodecylamine, didodecylamine, pentadecylamine, dipentadecylamine, tripentadecylamine, octadecylamine, dioctadecylamine, trioctadecylamine, and Primene[®] 81R which is a mixture of C_{11} to C_{14} tertiary alkyl primary amines available from Rohm & Haas.

[0038] The polyamine of (a)(ii)(3) can contain two or more amino groups where each amino group can be a primary, secondary or tertiary amino group. The polyamine of (a)(ii)(3) can be an alkylenediamine, a polyalkylenepolyamine such as a polyethylenepolyamine, or a mixture thereof. Useful examples of polyamines are ethylenediamine, propylenediamine, 1,3-diaminopropane, N-methylethylenediamine, diethylenetriamine, triethylenetetramine, tris(2-aminoethyl)amine, and polyethylenepolyamine bottoms.

[0039] The nitrogen containing heterocycle of (a)(ii)(4) can include a heterocycle having an aromatic and/or nonaro-

matic ring system that includes one or more nitrogen atoms. Often the ring system contains at least 5 or 6 atoms, although the ring systems may contain up to 15, in one aspect up to 12 and in yet another aspect up to 10 atoms. The number of nitrogen atoms in the ring system is often from 1 to 5, in one aspect 1 to 4 and in yet another aspect 1 to 3. The ring system may be substituted or unsubstituted, branched or unbranched. In one aspect the ring system is unsubstituted. The nitrogen containing heterocycle can include for example a pyrrole, a pyrrolidine, an imidazole, an imidazoline, a piperazine, a pyrazole, an oxazole, a pyridine, a piperidine, a pyrimidine, a purine, a benzotriazole, a 1,2,4-triazole, a quinoline, an isoquinoline, a carbazole or mixtures thereof. In one embodiment the nitrogen containing heterocycle is selected from the group consisting of a pyrrole, an imidazole, an imidazoline, a pyrazole and mixtures thereof.

[0040] The aminoalcohol of (a)(ii)(5) can contain one or more hydroxyl groups and one or more amino groups. The aminoalcohol in embodiments of this invention can contain 1 to 6 or 1 to 3 hydroxyl groups, 1 to 8 or 1 to 2 amino groups, and 2 to 50 or 2 to 40 or 2 to 25 or 2 to 15 carbon atoms. The aminoalcohol can be a monoalkanolamine, a dialkanolamine, a trialkanolamine or mixtures thereof. The aminoalcohol can include for example ethanolamine, isopropanolamine, diethanolamine, triethanolamine, N,N-diethylethanolamine, N,N-dimethylethanolamine, N,N-dibutylethanolamine, 3-amino-1,2-propanediol, serinol, 2-amino-2-methyl-1,3-propanediol, tris(hydroxymethyl)-aminomethane, diisopropanolamine, N-methyldiethanolamine, and 2-(2-aminoethylamino)ethanol.

[0041] The organic nitrogen-containing base may be (a)(ii)(6) a tetraalkylammonium salt. The tetraalkylammonium salt can have 4 or more carbon atoms. The tetraalkylammonium salt generally has a hydroxide anion or a reactive equivalent thereof to include a chloride, a carbonate, a bicarbonate, or a carboxylic acid anion such as formate or acetate. The tetraalkylammonium salt can be for example tetramethylammonium hydroxide or hexadecyltrimethylammonium hydroxide.

[0042] The non-heterocyclic aromatic amine of (a)(ii)(7) can contain one or more amino groups attached to a hydrocarbon aromatic ring system where the amino groups and ring system can be substituted or not substituted. The non-heterocyclic aromatic amine can include aminophenols, alkyl substituted aminophenols, phenylenediamines, and N-substituted phenylenediamines. The amine of (a)(ii)(7) can include for example aniline, 1,4-phenylenediamine, N-phenyl-1,4-phenylenediamine, N,N-dimethyl-1,4-phenylenediamine, and 2-amino-p-cresol.

[0043] In an embodiment of the invention the sulphur free reaction product of (a)(i) and (a)(ii) is a reaction product of (a)(i)(1) or (a)(i)(2) or mixtures thereof and (a)(ii)(1). In another embodiment of this invention the sulphur free reaction product is formed from (a)(i)(1) or (a)(i)(2) and (a)(ii)(1). In a further embodiment of the invention the sulphur free reaction product is formed from (a)(i)(1) and (a)(ii)(1). The sulphur free reaction product formed by reacting one or more members of component (a)(i) and an amino-containing imine of component (a)(ii)(1) is useful in the oil containing composition and methods of this invention.

Oils of Lubricating Viscosity

[0044] An oil of lubricating viscosity can be added to the sulphur free reaction product of (a)(i) and (a)(ii) of the present invention to form a composition which can be a lubricant composition such as an engine oil for an internal combustion engine. The oil of lubricating viscosity can be a natural oil, a synthetic oil, or a mixture thereof. Natural oils can include animal oils, plant oils, mineral oils from petroleum or coal or shale sources, and mixtures thereof. Mineral oils can include unrefined, refined and re-refined oils and mixtures thereof. Refined and re-refined mineral oils can include the American Petroleum Institute (API) Group I, II and III base oils. The oil of lubricating viscosity can include for example API Group III base oils such as Nexbase™ 3050, Nexbase™ 3043, Yubase™ 4, Yubase™ 6, Yurong™ 150N, Yurong™ 500N and Shell™ XHVI 5.2. Synthetic oils can include olefin polymers such as poly(alpha-olefin)s and hydrogenated poly(alpha-olefin)s, alkylated aromatics such as dodecylbenzene, carboxylic acid esters, and hydrocarbons from a gas-to-liquid process such as the Fischer-Tropsch process. The oil of lubricating viscosity can be present in the composition of the present invention on a weight basis at up to 99.99%, and in other embodiments at up to 99%, 95%, 90% or 80%.

Other Performance Additives

[0045] The composition of the present invention which contains the reaction product of (a)(i) and (a)(ii) can include other performance additives. The other performance additives can include metal deactivators such as benzotriazole derivatives, detergents such as sulphonates and phenates and carboxylates neutralized or overbased with metal bases, dispersants such as Mannich bases and succinimides generally prepared from polyisobutylenes having a number average molecular weight of 300 to 3000, antioxidants such as alkylated diphenylamines and hindered phenols and hindered phenol derivatives and mixtures thereof, antiwear agents to include zinc dialkyl dithiophosphates, corrosion inhibitors, antiscuffing agents, extreme pressure agents, foam inhibitors including silicone oils, demulsifiers, friction modifiers including amide and ester derivatives of fatty carboxylic acids, viscosity modifiers to include various polymeric viscosity index improvers and pour point depressants, seal swell agents, and mixtures thereof. Typically a fully formulated lubricating oil will contain one or more of these additives. The composition of the present invention, which comprises a sulphur

free reaction product of (a)(i) and (a)(ii) or the sulphur free reaction product and an oil of lubricating viscosity, can further comprise at least one other performance additive as described above, and in another embodiment of the invention can comprise at least one other performance additive selected from the group consisting of dispersants antioxidants, foam inhibitors, demulsifiers, friction modifiers, and viscosity modifiers. The other performance additive or additives can be present on a weight basis in a composition of the present invention at 0 to 30%, and in other embodiments can be present at 0.0001 to 30%, at 0.001 to 20%, or at 0.001 to 15%.

Process

[0046] The invention further provides a process for the preparation of a composition comprising:

(a) heating reactants (a)(i) and (a)(ii) often to a temperature of 50°C to 200°C, in one aspect at 60°C to 175°C, and in another aspect at 70°C to 150°C to form a product;

(b) optionally holding the product of step (a) under vacuum; and

(c) adding the product of step (a) or (b) to an oil of lubricating viscosity.

[0047] The reaction may be run using an oil of lubricating viscosity, water, alcohols, aliphatic and aromatic hydrocarbons such as toluene or xylene, or a mixture thereof to serve as a diluent and/or solvent. Solvents can be added anytime during the reaction process of steps (a) and (b). Diluents such as an oil can be added anytime before, during or after the reaction process.

[0048] In step (a), reactants (a)(i) and (a)(ii) can be combined and then the combination heated and stirred to form a product or a reactant can be heated and stirred and a second reactant added to the first reactant followed by heating and stirring to form a product. Often the reaction time is 30 seconds to 48 hours, in one aspect 2 minutes to 24 hours, in another aspect 5 minutes to 16 hours and in yet another aspect 10 minutes to 8 hours often at pressures of 86 kPa to 266 kPa (645 mm Hg to 2000 mm Hg), in one aspect 91 kPa to 200 kPa (690 mm Hg to 1500 mm Hg), and in another aspect 95 kPa to 133 kPa (715 mm Hg to 1000 mm Hg).

[0049] In step (b) the vacuum is often at pressures of 1 kPa to 85 kPa (7 mm Hg to 638 mm Hg), in one aspect 4 kPa to 70 kPa (30 mm Hg to 526 mm Hg) and in another aspect 6 kPa to 60 kPa (45 mm Hg to 450 mm Hg) for a period of time sufficient to substantially remove solvent and reaction by-products such as water.

[0050] The process optionally includes mixing other performance additives as described above at the end of step (a) and/or the end of step (b) or at any point during or after step (c).

[0051] An embodiment of the invention is a product prepared by the above described process of preparation comprising step (a) and optional steps (b) and (c).

[0052] When the composition of the present invention comprises the sulphur free reaction product and an oil of lubricating viscosity it can be termed an additive composition. Generally when this additive composition is combined with other performance additives the combination can be termed a concentrate composition although a concentrate composition can contain a single additive. The additive composition or concentrate composition can be further diluted with an oil to form a lubricant composition, such as an engine oil for an internal combustion engine, containing an additive or additives at a level sufficient to provide satisfactory performance. The oil level in an additive or concentrate composition for fluidity and handleability purposes will generally be on a weight basis 10 to 90%, and in other instances be 20 to 80%, or 30 to 70%.

Industrial Application

[0053] The composition of the present invention is useful in an internal combustion engine including a spark-ignited engine or a compression-ignited engine. Suitable examples of an engine include a diesel fuelled engine, a gasoline fuelled engine, a natural gas fuelled engine or a mixed gasoline/alcohol fuelled engine. The engine may contain an exhaust treatment device.

[0054] The composition of the present invention comprising a sulphur free reaction product of (a)(i) and (a)(ii) may or may not include metal containing detergents and can be present in sufficient amount to provide detergent performance to an internal combustion engine where the detergent performance can include neutralizing acids, preventing corrosion, removing deposits, suspending deposits and deposit precursors, preventing wear, preventing oxidation, improving exhaust emissions (since the sulphur free reaction product contributes no sulphur or phosphorus and at most only minor amounts of sulphated ash to the composition), or combinations thereof. In an embodiment of the invention a method for lubricating an internal combustion engine comprises supplying to the engine a composition comprising the sulphur free reaction product of (a)(i) and (a)(ii), and in another embodiment the supplied composition has a reduced level of sulphur, phosphorus and sulphated ash as described below. In a further embodiment of the invention a method to provide detergent performance to an internal combustion engine comprises supplying to the engine a composition comprising

the sulphur free reaction product of (a)(i) and (a)(ii), in another embodiment where the composition supplied to the engine has a reduced level of sulphur and phosphorus and sulphated ash as described below, and in a still another embodiment where the reaction product of (a)(i) and (a)(ii) contributes no sulphur, no phosphorus, and a minor amount of to no sulphated ash to the composition supplied to the engine.

[0055] An embodiment of the invention is a use of the composition of the invention comprising the sulphur free reaction product of (a)(i) and (a)(ii) for imparting to an internal combustion engine one or more properties selected from the group consisting of improved engine cleanliness, decreased oxidation, decreased wear, decreased emissions and decreased poisoning of exhaust emission catalysts, and in another embodiment of the use the composition has reduced levels of sulphur, phosphorus and sulphated ash as described below. A further embodiment of this invention is a use of the composition comprising the sulphur free reaction product of (a)(i) and (a)(ii) for imparting to an internal combustion engine an improvement in one or more performance properties selected from the group consisting of cleanliness, wear and exhaust emissions, and in another embodiment of the use the composition has reduced levels of sulphur, phosphorus and sulphated ash as described below.

[0056] Often the composition has a total sulphur content below 0.5 wt %, in one aspect below 0.3 wt %, in another aspect below 0.1 wt % and in yet another aspect near 0 wt %. Often the major source of sulphur in the composition of the invention is derived from diluent oil. Usually the diluent oil is used in the manufacturing processes used for preparing many known additives such as detergents or dispersants. Excluding the diluent oil, the composition of the invention often have a sulphur content of 700 ppm or less, in one aspect 600 ppm or less, in another aspect 300 ppm or less, in yet another aspect 100 ppm or less and in yet another aspect 50 ppm or less such as less than 30 ppm, 25 ppm or less, 20 ppm or less and 15 ppm or less. When sulphur from the diluent oil is included, the sulphur content of the composition is often increased by up to 800 ppm, in one aspect up to 600 ppm and in another aspect up to 400 ppm, for instance about 200 ppm or about 300 ppm. In one embodiment the sulphur is present from 1 ppm or 10 ppm to 50 ppm or 200 ppm. In one embodiment of the invention the composition is free of sulphur excluding sulphur derived from diluent oil.

[0057] Often the composition has a total phosphorus content below 0.1 wt %, in one aspect below 0.085 wt %, in another aspect below 0.07 wt %, in yet another aspect below 0.055 wt % and in yet another aspect below 0.05 wt % of the composition, such as 200 ppm or less, in one aspect 100 ppm or less, in another aspect 50 ppm or less and in yet another aspect 10 ppm or less. In one embodiment the phosphorus is present from 1 ppm or 10 ppm to 50 ppm or 200 ppm. In one embodiment of the invention the composition is free of phosphorus.

[0058] Often the composition has a total sulphated ash content below 1.5 wt %, in one aspect below 1.1 wt %, in another aspect below 1.0 wt %, in yet another aspect below 0.08 wt % and in yet another aspect below 0.05 wt % of the composition, such as 0.04 wt % or less, 0.03 wt % or less or 0.02 wt % or less. In one embodiment of the invention the composition contains ash present from 0.01 wt % to 0.03 wt %.

[0059] The following examples provide an illustration of the invention. These examples are nonexhaustive and are not intended to limit the scope of the invention.

EXAMPLES

Preparative Example A: Preparation of PIB Phenol-Formaldehyde-Salicylic Acid

[0060] A 2 litre reaction flask is charged with 475 g (0.739 mole, 1 eq) polyisobutenyl phenol derived from high vinylidene polyisobutylene with a number average molecular weight of 550 (GLISSOPAL®550 commercially available from BASF) and 330 g mineral oil (SN150) and heated to 30°C. Via a pressure equalising dropping funnel, 3.4 g of 50% aqueous KOH (0.030 mole, 0.04 eq) is added all at once. The materials are heated to 75°C followed by addition over 0.5 hour via a pressure equalising dropping funnel, 81.6 g 37% aqueous formaldehyde (formalin) (1.01 moles, 1.367 eq) followed by heating at 75°C for 2 hours until free formaldehyde measures less than 2% (by titration). To the reaction is charged 51.6 g salicylic acid (0.374 mole, 0.51 eq) and the reaction is heated to 140°C as quickly as possible (0.3 hour) while controlling reflux, draining water of reaction via a Dean Stark trap. The reaction is held at 140°C for 1.5 hours while collecting 58 ml water. The materials are vacuum stripped at 140°C/100 mm Hg (equivalent to 13kPa) over 0.5 hour. The clear and golden residue is the product. Yield = 857 g, % K = 0.093%. Mass spec, GPC and H¹ and C¹³ NMR indicate that the product consists of 2 methylene bridged polyisobutenyl phenol molecules methylene bridged to one salicylic acid. A more detailed description of the reaction process is given in Example 5 of International Publication WO03/018728, page 23.

Preparative Example B: Preparation of PIB Phenol-Formaldehyde-3,5-Dihydroxybenzoic acid

[0061] The process is the same as Preparative Example A except, 415.5g of polyisobutenyl phenol derived from high vinylidene polyisobutylene with a number average molecular weight of 550 (GLISSOPAL®550 commercially available from BASF) is used, 290 g mineral oil (SN150) and 50.5g of 3,5-dihydroxybenzoic acid is used instead of salicylic acid.

Preparative Example C: Preparation of PIB Phenol-Formaldehyde-4-Hydroxybenzoic Acid

[0062] The process is the same as Preparative Example B except, 45.2g of 4-hydroxybenzoic acid is used instead of 3,5-dihydroxybenzoic acid.

Preparative Example D: Preparation of PIB Phenol-Formaldehyde-Anthranilic acid

[0063] The process is the same as Preparative Example A except, 200g polyisobutenyl phenol derived from high vinylidene polyisobutylene with a number average molecular weight of 550 (GLISSOPAL®550 commercially available from BASF) is used, 306 g mineral oil (SN150) and 14.1 g of anthranilic acid instead of salicylic acid. Furthermore after the addition of anthranilic acid is carried out at 70°C (instead of 75°C used in preparative example A) followed by the addition of 85g of xylene.

Preparative Example E: Preparation of Dodecyl Phenol-Formaldehyde Salicylic acid

[0064] The process is the same as Preparative Example A except, 346 g dodecylphenol (propylene tetramer derived, 1.32 moles, 1 equivalent (eq)); 95.6 g salicylic acid (0.69 mole, 0.52 eq); 226.9 g of 36.7% by weight formaldehyde in water (formalin) (1.70 moles, 1.356 eq); 45 g 25% aqueous ammonia (0.65 mole, 0.5 eq), and 500 g toluene (solvent) are used. A more detailed description of the reaction process is given in Example 1 of International Publication WO03/018728, page 22.

Example 1: Phenol-Formaldehyde-Salicylic Acid and Aminoguanidine Bicarbonate

[0065] To a 1 litre flask, equipped with overhead stirrer and paddle, heating mantle, splash head, Dean-Stark trap and condenser equipped for water removal, pressure equalizing dropping funnel, thermocouple and thermal control unit, is added 450g of Preparative Example A (60% actives, 0.186 moles, 1 equivalent) and 70g of toluene. This is then heated to 85°C, at which point a slurry of aminoguanidine bicarbonate (38g, 0.28moles, 1.5 equivalents) and distilled water (80g, about 90°C to aid solubility in the slurry) is added slowly over 15 minutes via a pressure equalising funnel. The reaction turns cloudy. Water removal is observed almost instantaneously after addition of the slurry. The mixture is heated in 5°C stages to 130°C. The reaction is then held for 2 hours at 130°C under reflux. Solution clears at this point. Whilst warm, the product is filtered under vacuum through a pad of finely divided diatomaceous earth using a Buchner flask. Analysis of the product indicates a sulphated ash of 0.34% (corresponds to less than 0.01% of metal believed to be potassium residue from potassium hydroxide used in preparative example 1), TBN of 29 mg KOH/g sample, Kinematic Viscosity @ 100°C= 391 mm²/s (or cSt) and a nitrogen content of 2.9%.

Example 2: Phenol-Formaldehyde-Salicylic Acid and Ammonia (not according to the invention)

[0066] 400g of the product from Preparative Example A is heated to 80°C in a 1 litre flask fitted with a stirrer, a thermocouple and a nitrogen feed. The flask is then charged dropwise over 15 minutes with 95 cm³ of 2 molar ammonia dissolved in methanol. The flask is held at temperature for 1.5 hours before being vacuum distilled to remove methanol. The product has a TBN of 17.5 mg KOH/g sample and Kinematic Viscosity @ 100°C= 208.9 mm²/s (or cSt).

Example 3: Phenol-Formaldehyde-Salicylic Acid and Imidazole

[0067] 313g of the product from Preparative Example A is heated to 80°C in a 1 litre flask fitted with a stirrer, a thermocouple and a nitrogen feed. The flask is then charged with 17.7g of imidazole added in small portions before the addition of 80g of diluent oil. The flask is heated to 110°C for 10 minutes, followed by heating to 120°C for 1.5 hours and then heating to 140°C for 3 hours. The product is vacuumed stripped at 140°C/100 mm Hg (equivalent to 13kPa) for 3 hours. The product has a TBN of 15.1 mg KOH/g sample and a Kinematic Viscosity @ 100°C= 95 mm²/s (or cSt).

Example 4: Phenol-Formaldehyde-Salicylic Acid and Ethanolamine

[0068] 300g of the product from Preparative Example A is heated to 85°C in a 1 litre flask fitted with a stirrer, a thermocouple and a nitrogen feed. The flask is then charged dropwise over 10 minutes with 20.1g of ethanolamine. The flask is then heated to 145°C for 5 hours. The product is vacuumed stripped at 140°C/100 mm Hg (equivalent to 13kPa) until excess amine is removed. The product has a TBN of 26.8 mg KOH/g sample.

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Example 5: Phenol-Formaldehyde-Salicylic Acid and Diethanolamine

5 [0069] The process is the same as Example 4 except 500 g of the product of Preparative Example A and 92.1 g diethanolamine is used instead of ethanolamine. The product has a TBN of 78.5 mg KOH/g sample.

Example 6: Phenol-Formaldehyde-Salicylic Acid and Triethanolamine

10 [0070] The process is the same as Example 4 except 49.3 g triethanolamine is used instead of ethanolamine. The product has a TBN of 51.3 mg KOH/g sample.

Example 7: Alkylsalicylate and Triethanolamine (not according to the invention)

15 [0071] 200 g of dodecyl salicylic acid is heated to 80°C in a 500ml flask fitted with a stirrer, a thermocouple and a nitrogen line. The flask is then charged with 34.2 g of triethanolamine, added dropwise over a period of 15 minutes. 234 g of diluent oil is added before the flask is held at 80°C for 4 hours before being vacuumed stripped at 140°C/100 mm Hg (equivalent to 13kPa). The product has a TBN of 28 mg KOH/g sample and Kinematic Viscosity @ 100°C= 22.2 mm²/s (or cSt).

Example 8: Product of Preparative Example B and Triethanolamine

20 [0072] 200 g of the product of Preparative Example B is heated to 80°C in a 500 ml flask fitted with a stirrer, a thermocouple and a nitrogen line. The flask is then charged with 41.4 g of triethanolamine added dropwise over a period of 15 minutes. 60 g of diluent oil is added before increasing the temperature to 90°C for 10 minutes followed by heating to 100°C for 10 minutes. The flask is then heated to 120°C for 45 minutes followed by heating to 140°C for 4 hours. The flask is then vacuum stripped for up to 5 hours at 140°C/100 mm Hg (equivalent to 13kPa). The product has a TBN of 38.5 mg KOH/g sample and Kinematic Viscosity @ 100°C= 61 mm²/s (or cSt).

Example 9: Product of Preparative Example C and Triethanolamine

30 [0073] The process is the same as Example 8, except 25.2 g of the product of Preparative Example C is used instead of the product of preparative example 2. The product has a TBN of 30 mg KOH/g sample, Kinematic Viscosity @ 100°C= 132 mm²/s (or cSt).

Example 10: Product of Preparative Example D and Triethanolamine

35 [0074] The process is the same as Example 8, except 13.2g of the product of Preparative Example D is used instead of the product of Preparative Example B. The product has a TBN of 19.2 mg KOH/g sample and Kinematic Viscosity @ 100°C= 54 mm²/s (or cSt).

Example 11: Product of Preparative Example C and Guanidine Bicarbonate

40 [0075] 117 g of the product of Preparative Example C is heated to 80°C in a 500 ml flask fitted with a stirrer, a thermocouple and a nitrogen line. The flask is then charged with 6 g of water and 3.8 g of guanidine bicarbonate is added dropwise over a period of 20 minutes. 27 g of diluent oil is added before increasing the temperature to 90°C for 10 minutes followed by heating to 90°C for 10 minutes. The flask is then heated to 100°C for 10 minutes followed by heating to 120°C for 20 minutes and finally heated to 130°C for 90 minutes. The flask is then vacuum stripped for up to 2 hours at 130°C/100 mm Hg (equivalent to 13kPa). The product has a TBN of 8.3 mg KOH/g sample and Kinematic Viscosity @ 100°C= 56.9 mm²/s (or cSt).

Example 12: Product of Preparative Example E and Guanidine Bicarbonate

50 [0076] The process is the same as Example 12, except 11 g of guanidine bicarbonate, 100 g of the product of Preparative Example E and 16 g of water are used. The product has a TBN of 29.2 mg KOH/g sample and Kinematic Viscosity @ 100°C= 154 mm²/s (or cSt).

Example 13 Product of Phenol-Fornialdehyde-Salicylic Acid and Triethylamine

55 [0077] The process is the same as Example 8, except 250 g of the product of Preparative Example A, 10 g of triethyl-

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amine and 71 g of diluent oil are used. The product has a TBN of 5.5 mg KOH/g sample and Kinematic Viscosity @ 100°C= 65.3 mm²/s (or cSt).

Example 14: Phenol-Formaldehyde-Salicylic Acid and Polyamine

[0078] 500 g of the product from Preparative Example A, 11.9 g of calcium hydroxide are heated to 80°C in a 1 litre flask fitted with a stirrer, a thermocouple and a nitrogen feed. The flask is then charged with 20.3 g of triethylenetetraamine. The flask is then charged with an excess of 260 g of carbon dioxide added via a sparge tube. The flask is then heated to 160°C in 5°C increments. The product is vacuumed stripped at 160°C/338 mm Hg (equivalent to 45kPa) for 30 minutes. The product has a TBN of 81 mg KOH/g and a nitrogen content of 1.2 wt %.

Example 15: Phenol-Formaldehyde-Salicylic Acid and Guanidine Carbonate

[0079] The process is the same as example 1 except 404 g of the product of Preparative Example A is mixed with 103 g of toluene and 127 g of guanidine carbonate. The product has a TBN of 29 mg KOH/g and a nitrogen content of 2.3 wt %.

Reference Example 1: Oil of Lubricating Viscosity

[0080] An oil of lubricating viscosity is prepared with (a) 42.5 g of Nexbase™ 3050 oil, (b) 34.4 g of Nexbase™ 3043 oil, (c) on an oil free basis 0.4 g of an amine dispersant viscosity modifier, (d) on an oil free basis 2.8 g of polyisobutylene succinimide dispersants, (e) 5 g of antioxidants including a diphenylamine and a hindered phenol, (f) 0.7 g of an olefin copolymer viscosity modifier and (g) a glycerol monooleate friction modifier. The composition contains 0 wt % of calcium, 0 wt % of phosphorus, 0 wt % of sulphur and 0 wt % of zinc.

Invention Lubricating Oil Compositions

[0081] A number of lubricating oil compositions are prepared using 5 g of the product of Examples 1-13 mixed into the oil of lubricating viscosity derived from Reference Example 1. The lubricating oil composition formed containing Example 1 is titled "Lubricating Oil Composition Example 1", Example 2 is titled "Lubricating Oil Composition Example 2", etc. to Example 13, titled "Lubricating Oil Composition Example 13". The composition has a KV100 of 13.11 mm²/s (or cSt) and a sulphated ash content of 0 wt %.

[0082] Lubricating Oil Composition Example 14 is prepared by adding on an oil free basis 1.96 wt % of the product of Example 14 to a lubricating oil composition containing (a) on an oil free basis 6.45 wt % of dispersant, (b) on an oil free basis 1.83 wt % of detergent, (c) 3.15 wt % of antioxidants including a diphenylamine and a hindered phenol, (d) 0.76 wt % of zinc dialkyl dithiophosphate and (e) 85.85 wt % of a API Group II Jurong™ oil (69 wt % of the oil is Jurong™ 150N base oil and 31 wt% Jurong™ 500N base oil) of lubricating viscosity.

Reference Example 2: Top Tier European Passenger Car Oil Formulation

[0083] Reference Example 2 is a successful European top tier passenger car oil formulation containing zinc dithiophosphate. The elemental analysis of the oil formulation indicates a calcium content of 3307 ppm, a phosphorus content of 889 ppm, a sulphur content of 2645 ppm and a zinc content of 959 ppm. The oil formulation has a KV100 of 11.3 mm²/s (or cSt) and sulphated ash content of 1.26 wt %.

Reference Example 3

[0084] Reference Example 3 is the same lubricating oil composition as Lubricating Oil Composition Example 14 except that it does not contain the product of Example 14.

Test 1: HFRR of Lubricating Oil Composition Examples 1-13 and Reference Examples 1-2

[0085] Examples 1-13 and Reference Examples 1-2 are evaluated for wear performance in a programmed temperature high frequency reciprocating rig (HFRR) available from PCS Instruments. HFRR conditions for the evaluations are 200 g load, 75 minute duration, 1000 micrometer stroke, 20 Hertz frequency, and temperature profile of 15 minutes at 40°C followed by an increase in temperature to 160°C at a rate of 2°C per minute. Wear scar in micrometers and film formation as percent film thickness were then measured with lower wear scar values and higher film formation values indicating improved wear performance.

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[0086] The percent film thickness is based on the measurement of electrical potential between an upper and a lower metal test plate in the HFRR. When the film thickness is 100%, there is a high electrical potential for the full length of the 1000 micrometre stroke, suggesting no metal to metal contact. Conversely for a film thickness of 0% there is no electrical potential suggesting continual metal to metal contact between the plates. For intermediate film thicknesses, there is an electrical potential suggesting the upper and lower metal test plate have a degree of metal to metal contact as well as other areas with no metal to metal contact. The wear scar and film formation results obtained are presented in Table 1.

Table 1: Wear Scar and Film Formation Data

Example	Wear Scar (μm)	Film Formation
Lubricating Oil Composition Example 1	141	74
Lubricating Oil Composition Example 2*)	167	25
Lubricating Oil Composition Example 3	176	24
Lubricating Oil Composition Example 4	156	23
Lubricating Oil Composition Example 5	173	22
Lubricating Oil Composition Example 6	193	6
Lubricating Oil Composition Example 7*)	219	2
Lubricating Oil Composition Example 8	207	6
Lubricating Oil Composition Example 9	181	13
Lubricating Oil Composition Example 10	175	20
Lubricating Oil Composition Example 11	162	40
Lubricating Oil Composition Example 12	176	13
Lubricating Oil Composition Example 13	178	27
Reference Example 1	189	12
Reference Example 2	126	88
*) not according to the invention		

[0087] The analysis shows the compositions of the invention have antiwear performance and Example 1 is comparable with Reference Example 2.

Test 2: HFRR of Lubricating Oil Composition Example 14 and Reference Example 3

[0088] The apparatus used is the same as Test 1. However Example 14 and Reference Example 3 are treated with 1 wt % cumene hydroperoxide. The examples are then evaluated using the HFRR conditions a 500 g load, 75 minute duration, 1000 micrometer stroke, 20 Hertz frequency, and isothermal temperature profile at 105°C. The wear scar and film formation results obtained are presented in Table 2.

Table 2: Wear Scar and Film Formation Data

Example	Average Wear Scar (μm) from 3 HFRR Experiments	Film Formation
Lubricating Oil Composition Example 14	223	45
Reference Example 3	246	2

[0089] The analysis shows the composition containing Example 14 has on average a better antiwear result compared with Reference Example 3.

Test 3: Pressure Differential Scanning Calorimetry

[0090] A Pressure Differential Scanning Calorimetry (PDSC) test is carried out based on the Coordinating European

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Council (CEC) test method L-85-T-99. The results are based on the oxidation induction time. Better PDSC results are obtained for examples with higher oxidation induction times. The results obtained are:

Example	Oxidation induction Time (mins)
Reference Example 3	82.5
Lubricating Oil Composition Example 14	95

[0091] The analysis shows that the composition containing Example 14 has an improved oxidation induction time result compared with Reference Example 3.

Test 4: Komatsu Hot Tube

[0092] The Komatsu Hot Tube Test (KHT) uses glass tubes placed through aluminum heater block and heated to 280°C with an air flow of 10 cm³/min and an oil flow of 0.31 cm³/hr. The sample is pumped via a syringe pump through the glass tube for 16 hours. At end of test, the tubes are rinsed and weighed. The tube is also rated visually, using a 0-10 scale with 0 being a black tube and 10 a clean tube. The results obtained are:

Example	Deposit Control
Reference Example 3	2.5
Lubricating Oil Composition Example 14	9

[0093] The analysis shows the composition containing Example 14 has reduced deposit formation compared with Reference Example 3.

Test 5: Dispersant Dilution Test

[0094] The dispersant dilution test is reported as a sludge to chemical ratio which represents the lowest concentration of chemical to suspend an artificial sludge in an oil solution as described in U. S.-A- 4,146,489 and 5,814,586. Higher values for the tube number and ratio indicate that a chemical is more effective in suspending sludge. The results obtained are presented in Table 3.

Table 3: Sludge Dilution Test

Example	Tube Number	Sludge to Chemical Ratio
Reference Example 1	1	6
Lubricating Oil Composition Example 1	6	125
Lubricating Oil Composition Example 15	5	23

[0095] The results show that the compositions containing Examples 1 and 15 have improved dispersant properties compared with Reference Example 1.

[0096] Overall the composition of the invention improves engine cleanliness, decreases oxidation, decreases wear, decreases emissions and decreases poisoning of exhaust emission catalysts.

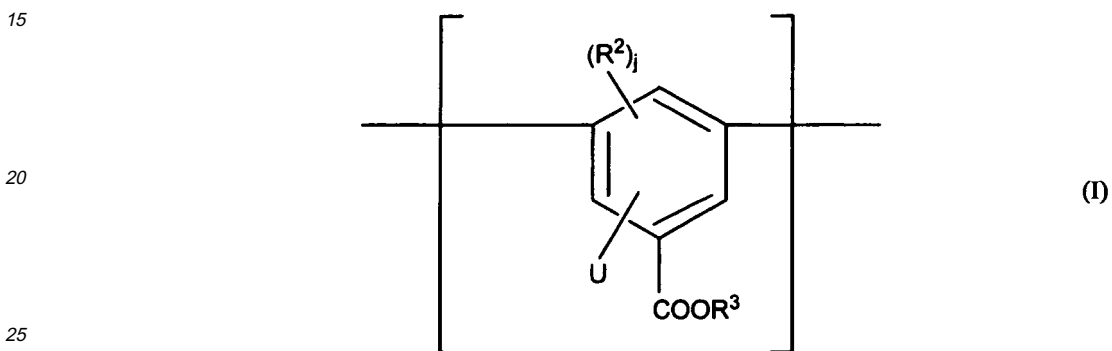
[0097] Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated.

[0098] As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

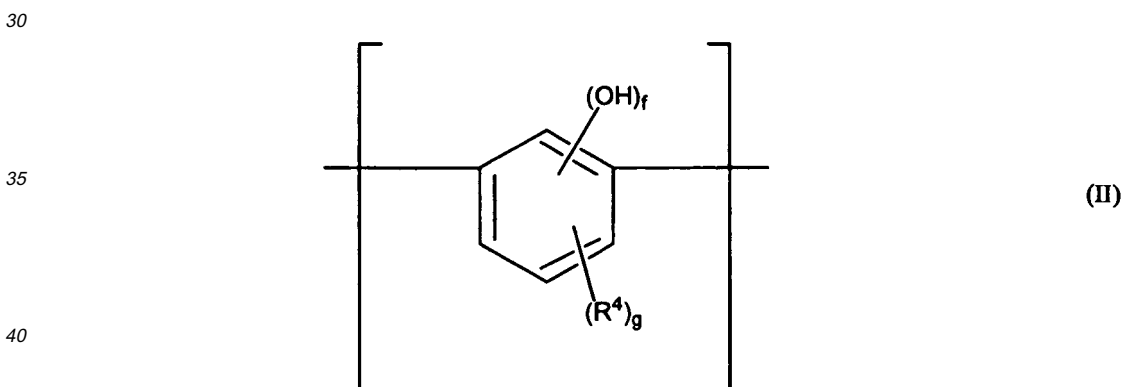
Claims

1. A composition comprising:

- 5 (a) a sulphur free reaction product of:
- (i) a hydrocarbyl substituted aromatic compound containing an acidic group selected from the group consisting of a carboxylic group, a hydroxyl group and mixtures thereof; and
 - 10 (ii) an organic nitrogen-containing base reacted with the acidic group; and
- (b) an oil of lubricating viscosity,
- wherein (a)(i) is a substantially linear compound comprising at least one unit of the formula (I)



or the formula (II)

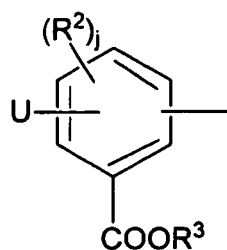


wherein each end of the compound is terminated by a unit of the formula (III) or the formula (IV)

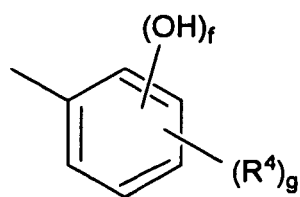
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(III)



(IV)

and wherein the units of the compound are linked by divalent bridging groups which may be the same or different for each linkage; U is a hydroxyl group for (a)(i)(1), or is selected from the group consisting of $-\text{NH}_2$, $-\text{NHR}^1$, $-\text{N}(\text{R}^1)_2$ and mixtures thereof for (a)(i)(2), wherein R^1 is a hydrocarbyl group containing 1 to 5 carbon atoms; R^2 is a hydroxyl or a hydrocarbyl group and j is 0, 1 or 2; R^3 is hydrogen or a hydrocarbyl group; R^4 is a hydrocarbyl group or a substituted hydrocarbyl group and g is 1, 2 or 3 provided that at least one R^4 group contains 8 or more carbon atoms; and wherein the compound on average contains at least one unit of formula (I) or (III) and at least one unit of formula (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the compound is 0.1:1 to 2:1.

2. The composition of claim 1 further comprising at least one other performance additive selected from the group consisting of dispersants, antioxidants, foam inhibitors, demulsifiers, friction modifiers, and viscosity modifiers.
3. The composition of claim 1, wherein component (a) is present at 0.01 wt % to 40 wt %; the oil of lubricating viscosity is present at up to 99.99 wt %; and wherein other performance additives are present at 0 wt % to 30 wt % of the composition.
4. The composition of claim 1, wherein the total sulphur content of the composition is below 0.5 weight percent; wherein the total phosphorus content of the composition is below 0.07 weight percent; and wherein the total sulphated ash content of the composition is below 1.5 weight percent.
5. The composition of claim 4, wherein the total sulphur content is below 0.1 weight percent; wherein the total phosphorus content is 100 ppm or less; and wherein the total sulphated ash content is below 0.08 weight percent.
6. The composition of claim 1, wherein (a)(ii) is at least one member selected from the group consisting of (1) an amino-containing imine or a reactive equivalent thereof; (2) a monoamine; (3) a polyamine; (4) a nitrogen containing heterocycle; (5) an aminoalcohol; (6) a tetraalkylammonium salt; and (7) a non-heterocyclic aromatic amine.
7. The composition of claim 6, wherein (a)(ii)(1) is at least one member selected from the group consisting of guanidine, aminoguanidine, 1,3-diaminoguanidine, acetamidine, formamidine, benzamidine, 3- and 4-aminobenzamidine, and reactive equivalents thereof.
8. The composition of claim 6, wherein (a)(ii)(2) is a hydrocarbyl substituted primary, secondary or tertiary monoamine or mixture thereof.
9. The composition of claim 6, wherein (a)(ii)(3) is an alkylenediamine, a polyethylenepolyamine, or a mixture thereof.
10. The composition of claim 6, wherein (a)(ii)(4) is a pyrrole, a pyrrolidine, an imidazole, an imidazoline, a piperazine, a pyrazole, an oxazole, a pyridine, a piperidine, a pyrimidine, a purine, a benzotriazole, a 1,2,4-triazole, a quinoline, an isoquinoline, a carbazole or mixtures thereof.
11. The composition of claim 6, wherein (a)(ii)(5) is an aminoalcohol containing 1 to 6 hydroxyl groups, 1 to 8 amino groups, and 2 to 50 carbon atoms.

12. The composition of claim 11, wherein the aminoalcohol is a monoalkanolamine, a dialkanolamine, a trialkanolamine or mixtures thereof.

13. The composition of claim 1, wherein component (a) is free of metal.

14. A process for the preparation of the composition of claim 1, comprising:

- (a) heating reactants (a)(i) and (a)(ii);
- (b) optionally holding the product of step (a) under vacuum; and
- (c) adding the product of step (a) or (b) to an oil of lubricating viscosity.

15. A product prepared by the process of claim 14.

16. A method for lubricating an internal combustion engine, comprising supplying to the engine the composition claim 1.

17. The use of the composition of claim 1 for imparting to an internal combustion engine an improvement in one or more performance properties selected from the group consisting of cleanliness, wear and exhaust emissions.

18. A composition comprising:

(a) a sulphur free reaction product of:

- (i) a hydrocarbyl substituted aromatic compound containing a carboxyl and/or hydroxyl acidic group and selected from the group consisting of (1) an oligomeric reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenol; (2) an oligomeric reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and a carboxyl-substituted phenylamine; and mixtures thereof; and
- (ii) an organic nitrogen-containing base reacted with the acidic group of (a)(i).

Patentansprüche

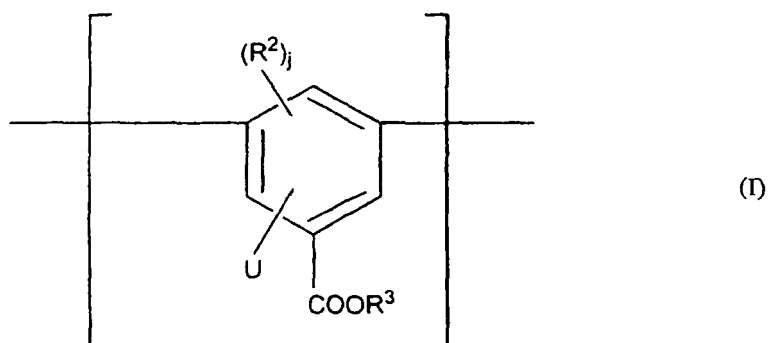
1. Zusammensetzung, umfassend:

(a) ein schwefelfreies Reaktionsprodukt von:

- (i) einer hydrocarbylsubstituierten aromatischen Verbindung, die eine saure Gruppe enthält, die aus der Gruppe ausgewählt ist, die aus einer Carboxygruppe, einer Hydroxygruppe und Gemischen davon besteht; und
- (ii) einer organischen stickstoffhaltigen Base, die mit der sauren Gruppe umgesetzt wird; und

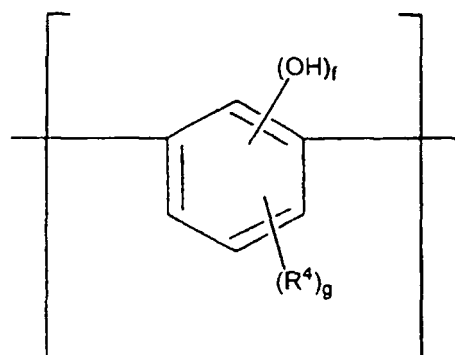
(b) ein Öl mit Schmierviskosität;

wobei (a)(i) eine im Wesentlichen lineare Verbindung ist, die wenigstens eine Einheit der Formel (I)



oder der Formel (II)

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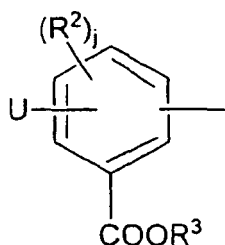
(II)

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umfasst, wobei jedes Ende der Verbindung durch eine Einheit der Formel (III) oder der Formel (IV)

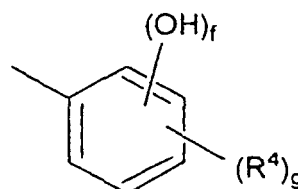
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(III)



(IV)

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abgeschlossen ist und wobei die Einheiten der Verbindung durch zweiwertige Verbrückungsgruppen miteinander verknüpft sind, die für jede Bindung gleich oder verschieden sein können, U für (a)(i)(1) eine Hydroxygruppe ist oder für (a)(i)(2) aus der Gruppe ausgewählt ist, die aus $-NH_2$, $-NHR^1$, $-N(R^1)_2$ und Gemischen davon besteht, wobei R^1 eine Hydrocarbylgruppe ist, die 1 bis 5 Kohlenstoffatome enthält, R^2 eine Hydroxy- oder Hydrocarbylgruppe ist und $j = 0, 1$ oder 2 ist, R^3 Wasserstoff oder eine Hydrocarbylgruppe ist, $f = 1, 2$ oder 3 ist, R^4 eine Hydrocarbylgruppe oder eine substituierte Hydrocarbylgruppe ist und $g = 1, 2$ oder 3 ist, mit der Maßgabe, dass wenigstens eine R^4 -Gruppe 8 oder mehr Kohlenstoffatome enthält, und wobei die Verbindung im Durchschnitt wenigstens eine Einheit der Formel (I) oder (III) und wenigstens eine Einheit der Formel (II) oder (IV) enthält und das Verhältnis der Gesamtzahl der Einheiten (I) und (III) zur Gesamtzahl der Einheiten (II) und (IV) in der Verbindung 0,1:1 bis 2:1 beträgt.

2. Zusammensetzung gemäß Anspruch 1, die weiterhin wenigstens ein weiteres Performance-Additiv umfasst, das aus der Gruppe ausgewählt ist, die aus Dispergiermitteln, Antioxidantien, Schaumhhibitoren, Demulgatoren, Reibungsmodifikatoren und Viskositätsmodifikatoren besteht.
3. Zusammensetzung gemäß Anspruch 1, wobei Komponente (a) in einem Anteil von 0,01 Gew.-% bis 40 Gew.-% vorhanden ist, das Öl mit Schmierviskosität in einem Anteil von bis zu 99,99 Gew.-% vorhanden ist und wobei weitere Performance-Additive in einem Anteil von 0 Gew.-% bis 30 Gew.-% der Zusammensetzung vorhanden sind.
4. Zusammensetzung gemäß Anspruch 1, wobei der Gesamtschwefelgehalt der Zusammensetzung unter 0,5 Gew.-% liegt, wobei der Gesamtphosphorgehalt der Zusammensetzung unter 0,07 Gew.-% liegt und wobei der Gesamtgehalt der Zusammensetzung an sulfatierter Asche unter 1,5 Gew.-% liegt.
5. Zusammensetzung gemäß Anspruch 4, wobei der Gesamtschwefelgehalt unter 0,1 Gew.-% liegt, wobei der Ge-

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samtposphorgehalt 100 ppm oder weniger beträgt und wobei der Gesamtgehalt an sulfatierter Asche unter 0,08 Gew.-% liegt.

- 5 6. Zusammensetzung gemäß Anspruch 1, wobei (a)(ii) wenigstens ein Element ist, das aus der Gruppe ausgewählt ist, die aus (1) einem aminohaltigen Imin oder einem reaktiven Äquivalent davon, (2) einem Monoamin, (3) einem Polyamin, (4) einem stickstoffhaltigen Heterocyclus, (5) einem Aminoalkohol, (6) einem Tetraalkylammoniumsalz und (7) einem nichtheterocyclischen aromatischen Amin besteht.
- 10 7. Zusammensetzung gemäß Anspruch 6, wobei (a)(ii)(1) wenigstens ein Element ist, das aus der Gruppe ausgewählt ist, die aus Guanidin, Aminoguanidin, 1,3-Diaminoguanidin, Acetamidin, Formamidin, Benzamidin, 3- und 4-Aminobenzamidin und reaktiven Äquivalenten davon besteht.
- 15 8. Zusammensetzung gemäß Anspruch 6, wobei (a)(ii)(2) ein hydrocarbylsubstituiertes primäres, sekundäres oder tertiäres Monoamin oder ein Gemisch davon ist.
- 20 9. Zusammensetzung gemäß Anspruch 6, wobei (a)(ii)(3) ein Alkylendiamin, ein Polyethylenpolyamin oder ein Gemisch davon ist.
- 25 10. Zusammensetzung gemäß Anspruch 6, wobei es sich bei (a)(ii)(4) um ein Pyrrol, ein Pyrrolidin, ein Imidazol, ein Imidazolin, ein Piperazin, ein Pyrazol, ein Oxazol, ein Pyridin, ein Piperidin, ein Pyrimidin, ein Purin, ein Benzotriazol, ein 1,2,4-Triazol, ein Chinolin, ein Isochinolin, ein Carbazol oder Gemische davon handelt.
- 30 11. Zusammensetzung gemäß Anspruch 6, wobei (a)(ii)(5) ein Aminoalkohol ist, der 1 bis 6 Hydroxygruppen, 1 bis 8 Aminogruppen und 2 bis 50 Kohlenstoffatome enthält.
- 35 12. Zusammensetzung gemäß Anspruch 11, wobei es sich bei dem Aminoalkohol um ein Monoalkanolamin, ein Dialkanolamin, ein Trialkanolamin oder Gemische davon handelt.
- 40 13. Zusammensetzung gemäß Anspruch 1, wobei Komponente (a) frei von Metall ist.
- 45 14. Verfahren zur Herstellung der Zusammensetzung von Anspruch 1, umfassend:
- (a) Erhitzen der Reaktanten (a)(i) und (a)(ii);
 - (b) gegebenenfalls Halten des Produkts von Schritt (a) unter Vakuum; und
 - (c) Hinzufügen des Produkts von Schritt (a) oder (b) zu einem Öl mit Schmierviskosität.
- 50 15. Produkt, hergestellt nach dem Verfahren von Anspruch 14.
- 55 16. Verfahren zur Schmierung eines Verbrennungsmotors, umfassend das Zuführen der Zusammensetzung von Anspruch 1 zu dem Motor.
17. Verwendung der Zusammensetzung von Anspruch 1 zum Verbessern einer oder mehrerer Leistungseigenschaften eines Verbrennungsmotors, die aus der Gruppe ausgewählt sind, die aus Sauberkeit, Verschleiß und Abgasemissionen besteht.
18. Zusammensetzung, umfassend:
- (a) ein schwefelfreies Reaktionsprodukt von:
 - (i) einer hydrocarbylsubstituierten aromatischen Verbindung, die eine saure Carboxygruppe und/oder Hydroxygruppe enthält und aus der Gruppe ausgewählt ist, die aus (1) einem oligomeren Reaktionsprodukt eines hydrocarbylsubstituierten Phenols, eines Aldehyds und eines carboxysubstituierten Phenols, (2) einem oligomeren Reaktionsprodukt eines hydrocarbylsubstituierten Phenols, eines Aldehyds und eines carboxysubstituierten Phenylamins und Gemischen davon besteht; und
 - (ii) einer organischen stickstoffhaltigen Base, die mit der sauren Gruppe von (a)(i) umgesetzt wird.

Revendications

1. Composition, comprenant:

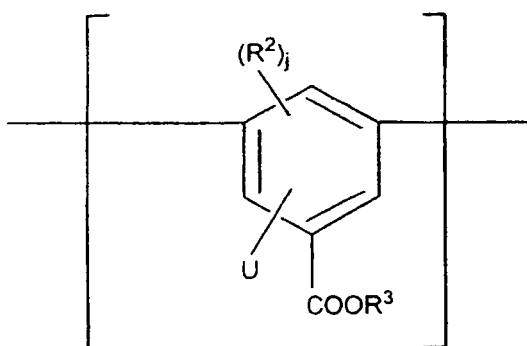
5 (a) un produit de réaction exempt de soufre de:

- (i) un composé aromatique substitué par hydrocarbyle qui contient un groupe acide choisi dans le groupe consistant en un groupe carboxylique, un groupe hydroxyle et des mélanges de ceux-ci; et
- (ii) une base contenant de l'azote organique, que l'on a fait réagir avec le groupe acide; et

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(b) une huile à viscosité lubrifiante;
 dans laquelle (a)(i) est un composé sensiblement linéaire comprenant au moins un motif de la formule (I)

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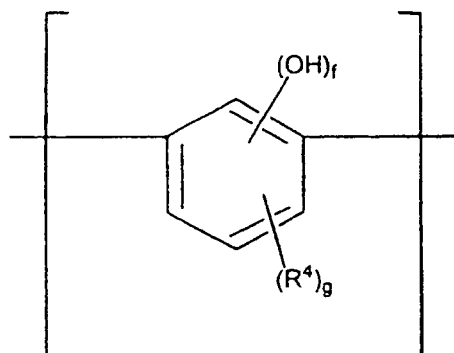
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(I)

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ou de la formule (II)

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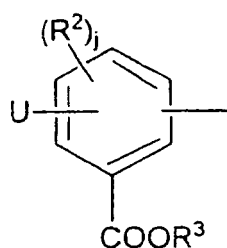
(II)

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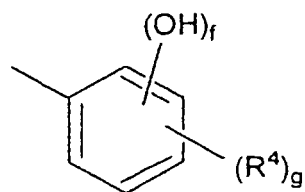
45 dans lesquelles chaque extrémité du composé est terminée par un motif de la formule (III) ou de la formule (IV)

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(III)



(IV)

et dans lesquelles les motifs du composé sont liées l'un à l'autre par des groupes de pontage divalents qui peuvent être identiques ou différents pour chaque liaison; U est un groupe hydroxyle pour (a)(i)(1) ou est choisi dans le groupe consistant en $-NH_2$, $-NHR^1$, $-N(R^1)_2$ et des mélanges de ceux-ci pour (a)(i)(2), où R^1 est un groupe hydrocarbyle contenant de 1 à 5 atomes de carbone, R^2 est un groupe hydroxyle ou hydrocarbyle et j vaut 0, 1 ou 2, R^3 est hydrogène ou un groupe hydrocarbyle, f vaut 1, 2 ou 3, R^4 est un groupe hydrocarbyle ou un groupe hydrocarbyle substitué et g vaut 1, 2 ou 3, à condition qu'au moins un groupe R^4 contienne au moins 8 atomes de carbone, et dans laquelle le composé contient en moyenne au moins un motif de la formule (I) ou (III) et au moins un motif de la formule (II) ou (IV), et le rapport du nombre total des motifs (I) et (III) au nombre total des motifs (II) et (IV) dans le composé est de 0,1:1 à 2:1.

2. Composition selon la revendication 1, comprenant en outre au moins un autre additif de performance choisi dans le groupe consistant en des dispersants, des antioxydants, des inhibiteurs de mousse, des démulsiants, des modificateurs de friction et des modificateur de viscosité.
3. Composition selon la revendication 1, dans laquelle le composant (a) est présent à raison de 0,01 % en poids à 40 % en poids, l'huile à viscosité lubrifiante est présente à raison de jusqu'à 99,99 % en poids, et dans laquelle d'autres additifs de performance sont présents à raison de 0 % en poids à 30 % en poids de la composition.
4. Composition selon la revendication 1, dans laquelle la teneur totale en soufre de la composition est moins de 0,5 pour cent en poids, dans laquelle la teneur totale en phosphore de la composition est moins de 0,07 pour cent en poids, et dans laquelle la teneur totale en cendre sulfatée de la composition est moins de 1,5 pour cent en poids.
5. Composition selon la revendication 4, dans laquelle la teneur totale en soufre est moins de 0,1 pour cent en poids, dans laquelle la teneur totale en phosphore est 100 ppm ou moins, et dans laquelle la teneur totale en cendre sulfatée est moins de 0,08 pour cent en poids.
6. Composition selon la revendication 1, dans laquelle (a)(ii) est au moins un élément choisi dans le groupe consistant en (1) une imine contenant des groupes amino ou un équivalent réactif de celle-ci, (2) une monoamine, (3) une polyamine, (4) un hétérocycle contenant de l'azote, (5) un aminoalcool, (6) un sel de tétraalkylammonium et (7) une amine aromatique non hétérocyclique.
7. Composition selon la revendication 6, dans laquelle (a)(ii)(1) est au moins un élément choisi dans le groupe consistant en guanidine, aminoguanidine, 1,3-diaminoguanidine, acétamidine, formamidine, benzamidine, 3-et 4-aminobenzamidine et des équivalents réactifs de ceux-ci.
8. Composition selon la revendication 6, dans laquelle (a)(ii)(2) est une monoamine primaire, secondaire ou tertiaire substituée par hydrocarbyle ou une mélange de celles-ci.
9. Composition selon la revendication 6, dans laquelle (a)(ii)(3) est une alkylènediamine, une polyéthylène polyamine ou un mélange de celles-ci.
10. Composition selon la revendication 6, dans laquelle (a)(ii)(4) est un pyrrole, une pyrrolidine, un imidazole, une imidazoline, une piperazine, un pyrazole, un oxazole, une pyridine, une piperidine, une pyrimidine, une purine, un

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benzotriazole, un 1,2,4-triazole, une quinoline, une isoquinoline, un carbazole ou des mélanges de ceux-ci.

5 11. Composition selon la revendication 6, dans laquelle (a)(ii)(5) est un aminoalcool contenant 1 à 6 groupes hydroxyle, 1 à 8 groupes amino et 2 à 50 atomes de carbone.

12. Composition selon la revendication 11, dans laquelle ledit aminoalcool est une monoalkanolamine, une dialkanolamine, une trialkanolamine ou des mélanges de ceux-ci.

10 13. Composition selon la revendication 1, dans laquelle le composant (a) est exempt de métal.

14. Procédé pour préparer la composition de la revendication 1, comprenant les étapes consistant à:

(a) chauffer les réactifs (a)(i) et (a)(ii);

(b) éventuellement maintenir le produit de l'étape (a) sous vide; et

15 (c) ajouter le produit de l'étape (a) ou (b) à une huile à viscosité lubrifiante.

15. Produit préparé par le procédé de la revendication 14.

20 16. Procédé de lubrification d'un moteur à combustion interne, comprenant l'étape consistant à alimenter la composition de la revendication 1 au moteur.

25 17. Utilisation de la composition de la revendication 1 pour apporter au moteur à combustion interne une amélioration d'une ou plusieurs qualités de performance choisi dans le groupe consistant en propreté, usure et émissions d'échappement.

18. Composition, comprenant:

(a) un produit de réaction exempt de soufre de:

30 (i) un composé aromatique substitué par hydrocarbyle qui contient un groupe acide carboxylique et/ou hydroxyle, choisi dans le groupe consistant en (1) un produit de réaction oligomérique d'un phénol substitué par hydrocarbyle, d'un aldéhyde et d'un phénol substitué par carboxyle, (2) un produit de réaction oligomérique d'un phénol substitué par hydrocarbyle, d'un aldéhyde et d'une phénylamine substituée par carboxyle, et des mélanges de ceux-ci; et

35 (ii) une base contenant de l'azote organique, que l'on a fait réagir avec le groupe acide de (a)(i).

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REFERENCES CITED IN THE DESCRIPTION

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